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Supplementary Material
for
Oxidation Chemistry of d^0 Organometallic Complexes

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Experimental Considerations

All manipulations were carried out under inert atmosphere conditions using standard drybox and Schlenk line techniques with dry, deoxygenated solvents. Methylene chloride and acetonitrile, as well as their deuterated counterparts used for NMR studies, were distilled under high vacuum from CaH_2 after deoxygenation by multiple freeze-pump-thaw cycles. Tetrabutylammonium tetraphenylborate (Aldrich) and tetrabutylammonium tetrafluoroborate were recrystallized from acetone/water (3/1) and acetonitrile/ethyl acetate, respectively, then dried in vacuo for several days. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, Aldrich) was recrystallized and dried in vacuo. Ferrocenium salts were prepared from ferrocenium tetrachloroferrate (Alfa). Tetrakis(trifluoromethyl)cyclopentadienone was prepared using literature methods[1] and purified by vacuum sublimation.

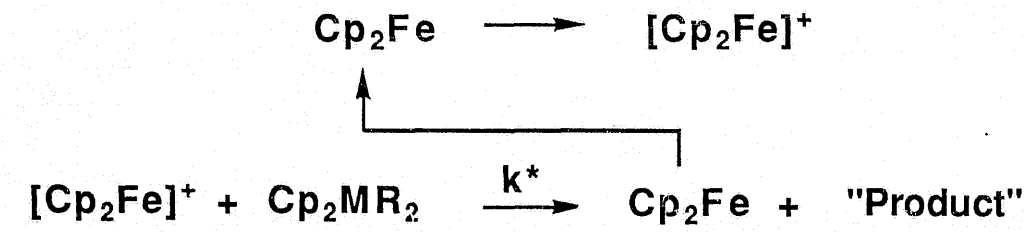
All metallocene dialkyl, diaryl, and metallacycle complexes used in this study were prepared according to literature procedures, purified by recrystallization, and characterized by nmr spectroscopy. The bis(cyclopentadienyl)titanacyclobutanes **1** and their stereolabelled analogs **4** were prepared from the Tebbe reagent and appropriate olefin following literature procedures.[2] Diphenyltitanocene[3] (**3**) and

diphenylzirconocene[4] (**2**) were obtained from phenyllithium (Aldrich) and the respective metallocene dichlorides (Aldrich), while the dibenzyl compounds **5** and **6** were prepared from Cp_2MCl_2 and benzylmagnesium chloride (Aldrich).[5,6] Dimethylzirconocene[4] was purified by vacuum sublimation (65 °C, 10^{-3} Torr). All samples used in this study were pure by NMR.

Electrochemical Experiments. Bulk electrolysis, cyclic voltammetry and rotating disk experiments were performed in a nitrogen filled drybox (Vac Atmospheres) or in airless electrochemical cells using a Princeton Applied Research (PAR) 173/175 programmer/potentiostat. Rotating disk experiments were perfomed with a Pine Instruments rotator and a Pt disk electrode in a teflon sheath. Microelectrode experiments were conducted using a homemade fast scan potentiosat and a Nicolet 3091 digital oscilloscope. Pt electrodes ($A = 0.029$ cm^2), microelectrodes ($r = 5$ μm), and Ag/AgCl reference electrodes were obtained from Bioanalytical Systems (BAS). $Ag/AgNO_3$ (0.1 M in CH_3CN) reference electrodes were used for all electrochemical experiments performed in the glove box. Microelectrode experiments were performed in an airless electrochemical cell with a Ag/AgCl reference electrode (BAS). Ferrocene ($E^o = +0.41$ V vs. SCE)[7] was added as an internal standard to verify potentials. Reported reduction potentials (Table 1) were then corrected to V vs. SCE. The electrochemical behavior of most of these complexes was very sensitive to adventitious water and/or oxygen; therefore, it was necessary to work under rigorously inert conditions. Cyclic voltammetry revealed that passivation of the platinum electrode occurred upon potential excursions into the anodic wave of the Cp_2MR_2 complexes. This was especially evident in ultramicroelectrode studies, even at scan rates of 1000 mV s^{-1}. Thus, determination of the $E_{1/2}$ values at very fast scan rates, where kinetic factors would presumably be minimized, were not generally feasible. It was necessary to clean the electrode

frequently to obtain consistent cyclic voltammograms. One exception to this was titanacyclobutane **1a**: at scan rates of 1000 V s^{-1}, the measured $E_{1/2}$ was 0.86 V vs SCE. The observation that this number was significantly positive of the value determined at a conventional electrode is consistent with a very fast chemical reaction following the oxidation of **1a**.

Electrochemical Mediation Experiments/ Kinetic Analysis. Cyclic voltammetric determinations of the reaction rates of the ferrocenium-mediated oxidation of Group 4 metallocene complexes were carried out in the glove box with either 7 or 15 equivalents of the metal alkyl (relative to the ferrocene). The data were analyzed according to an EC' scheme:[8]



by measuring i_∞ values. These limiting currents are related to the rate constant by

$$i_\infty = nFAC_o(Dk^*C_z)^{1/2}$$

which upon rearrangement affords

$$k^* = \left(\frac{i_\infty}{nFAC_o}\right)^2 \frac{1}{DC_z}$$

where k* is the bimolecular rate constant for the reaction between the ferrocenium ion and metal alkyl, i_∞ is the limiting current obtained directly from the cyclic

voltammogram, C_o is the ferrocene concentration, D is the ferrocene diffusion coefficient and C_z is the metal alkyl concentration.

Rotating Disk Experiments. The heterogeneous electron transfer rate for **1a** was determined by measuring the limiting currents at different applied potentials (vs. Ag/AgNO3 in Bu_4NBF_4/CH_3CN). The rate constant at a given potential, k_e, was determined using

$$k_e = i_e/nFAC_z$$

where i_e was estimated from the limiting current at the highest rotation rates (3600 RPM) or from the intercept of inverse Levich plots (1/i vs. $\omega^{-1/2}$). Kinetic measurements on metallocene compounds other than **1a** were hampered by electrode passivation.

Product Analyses of Bulk Electrolyses. Bulk electrolyses of several compounds for the purpose of product analysis were performed in deuterated solvents using a U-cell with a frit to separate the working and counter electrode solutions. In a typical experiment, ca. 100 mg of metallocene complex **1**, **2**, **3**, or **4** was dissolved in 4 ml deuterated solvent (CD_2Cl_2 or CD_3CN) along with electrolyte (0.1 M) in the working side of the cell (Pt gauze working electrode). The counter electrode was a Pt foil in 0.1 M electrolyte. In order to avoid complications from competing thermal retro 2+2 cleavage, electrolysis experiments on the titanacyclobutanes **1a** and **4** were run at 0 °C in airless electrochemical cells. The working electrode contents were then transferred under Ar to a schlenk tube via cannula. After several freeze-pump-thaw cycles, the volatiles were collected by vacuum transfer at 0 °C and analyzed by NMR. This procedure prevented the production of alkenes from thermal decomposition[2] and revealed exclusive production of cyclopropanes. The stereochemistry of the deuterated cyclopropanes formed by oxidation of **4** was determined by integration of

the methylene resonances (^{1}H NMR).[9] For the diphenylmetallocenes **2** and **3**, bulk electrolyses were performed at room temperature in the drybox and the products (biphenyl and/or benzene) were characterized by ^{1}H NMR analysis of the working electrode solutions. Electrode passivation was a considerable problem for **2** and **3** during oxidative electrolysis, preventing high conversions and thereby hampering product analysis. Complex **2** was found to be very sensitive to partial hydrolysis resulting in the production of $(Cp_2ZrPh)_2O$ and benzene during electrolysis. We were unable to discern whether the benzene produced from electrolysis of **2** was due solely to hydrolysis or also resulted from oxidative cleavage as well. Nonetheless the electrolytic production of benzene and biphenyl corroborate an electron transfer process.

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